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Bounds on transport coefficients of random polycrystals of laminates are presented, including the well-known Hashin-Shtrikman bounds and some newly formulated bounds involving two formation factors for a two-component porous medium. Some new types of self-consistent estimates are then formulated based on the observed analytical structure both of these bounds and also of earlier self-consistent estimates (of the CPA or coherent potential approximation type). A numerical study is made, assuming first that the internal structure (*i.e.*, the laminated grain structure) is not known, and then that it is known. The purpose of this aspect of the study is to attempt to quantify the differences in the predictions of properties of a system being modelled when such organized internal structure is present in the medium but detailed spatial correlation information may or (more commonly) may not be available. Some methods of estimating formation factors from data are also presented and then applied to a high-contrast fluid-permeability data set. Hashin-Shtrikman bounds are found to be very accurate estimates for low contrast heterogeneous media. But formation factor lower bounds are superior estimates for high contrast situations. The new self-consistent estimators also tend to agree better with data than either the bounds or the CPA estimates, which themselves tend to overestimate values for high contrast conducting composites.

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I. INTRODUCTION

Effective medium theories have traditionally been formulated using physical arguments to arrive at thought experiments leading to definite predictions about the behavior of complex systems [1–4]. A small subset of these formulations [5–7] has been shown to correspond to realizable (at least in principle) microstructures and, therefore, to the conclusion that these approximations should always satisfy any rigorous bounds known for the physical constants. But, such realizability conditions are *not* always easy to establish and are *invariably* subject to the criticism [8] that, even though the implicit microstructure is realizable, it is nevertheless *not the pertinent microstructure* for the system we need to study either in the laboratory or in the field. Such realizable effective medium theories instead must typically have hierarchical microstructures [5], requiring many levels (often infinitely many in order to be space filling) for validity of the required separation of scales.

On the other hand, bounding methods obviously have the great advantage of rigor, but the disadvantage that, for real material constants and at each fixed choice of volume fraction, there are two numbers generated (upper and lower bounds), while for complex material constants (including both energy storage and dissipation), a closed curve in the complex plane describing the bounds is required (see, for example, [9–11]). But, for practical applications, users of such theories often want estimates rather than bounds — even though estimates together with additional measures of the probable range of errors in those estimates are also clearly advantageous for many applications. Nevertheless, it seems certain that, if bounds are available, then useful estimates can always be found. Hill [12] resolved this dilemma famously by suggesting the averaging (*i.e.*, using either the mean or the geometric mean) of the well-known Voigt and Reuss bounds for elastic constants, thereby producing the very well-known Voigt-Reuss-Hill estimates in elasticity [13, 14]. In other cases, known effective medium estimates have already been shown to lie between the bounds, but in fact if the analytical form of the bounds had been known first, then in many cases these common estimates could have very easily been deduced directly from the analytical form of the bounds [15].

The author has recently shown [16] how the Peselnick and Meister bounds (on elastic constants for polycrystals having grains with hexagonal symmetry [17]) applied to random polycrystals of laminates can be used to provide both bounds and self-consistent estimates of the shear modulus in the special case of heterogeneous elastic media having constant bulk modulus. The present paper will continue such studies in a different context by considering transport coefficients, including electrical conductivity, thermal conductivity, and fluid permeability of porous media. Some newly formulated bounds on conductivity [18] involving two formation factors for a

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two-component porous medium are also discussed and used to estimate formation factors from data and then to show that these lower bounds are superior to the Hashin-Shtrikman lower bounds for transport properties at high contrast.

The next section discusses and motivates the model of random polycrystals of laminates that we are exploring. Then Section III reviews some known bounds on the transport coefficients and presents two derivations of some new bounds available in porous media when formation factor information is available. This section also shows how to obtain information about formation factor from a data set if the formation factor itself has not been measured independently. Section IV reviews some standard estimates and presents some new ones based on the analytical form of both bounds and some previous estimates. Section V presents and discusses some numerical examples of applications of the estimates and bounds, and also comparisons to high contrast fluid permeability data. Section VI summarizes our conclusions. Appendix A discusses two methods of estimating formation factors from data, when none of the data happens to lie in the asymptotic range (*i.e.*, none is for very high or very low conductivity constituents, which are the limits best suited for direct formation factor estimates). Appendix B collects some details of the calculations needed in the main text.

II. DESCRIPTION OF THE UP-SCALING MODEL

One of the most common problems with all up-scaling methods for heterogeneous media is that it is most difficult to know — especially in quantitative terms — just how important various assumptions that are made during the up-scaling procedure are to the final results obtained. Clearly it is advantageous, but in the past has seldom been practical, to have an up-scaling model that provides natural means for estimating the range of errors generated when using the resulting model. We are usually most fortunate to have either bounds or estimates (by which we mean effective medium theory estimates) that can be computed for a given data set. In only a very limited number of cases do we have both bounds and estimates. And the most popular estimates themselves may not be consistent with the rigorous bounds in all cases.

With this dilemma in mind, we propose to make use of the following model: Suppose that at the macroscale we have an isotropic composite that is a random polycrystal, *i.e.*, an aggregate of randomly oriented crystals, each of which has the same anisotropic effective constants for elasticity, or electrical conductivity, or fluid permeability, or whatever physical quantity we need to study. We assume (for the purposes of model studies only, as we have no reason to think this model represents any real physical system, unless it has been specially engineered to be so) that the crystals themselves are composed of layers of isotropic materials. These crystals can come in any size, and they may not be layered identically at the microscale. But the model assumption is that each crystal has the same anisotropic constants. When considering quasi-statics or long-wavelength behavior in elasticity and also for transport coefficients, it is well-known that *it does not matter* exactly what order the layers are grouped in, or exactly how thick each layer is, etc. But *it does matter* that, for each crystal that composes the polycrystal, the corresponding volume fractions are the same. Furthermore, these crystalline aggregates at the mesoscale are assumed to be layered at a small enough microscale so that sufficient scale separation is a good assumption. This simply means that edge (or boundary) effects at the interfaces between contiguous grains can be safely neglected.

If we choose to do so, we can continue this hierarchy by supposing that each of the isotropic layers is itself composed of a very much finer microstructure. This next level of hierarchy is actually important for some of the modeling we have in mind. In particular for porous media, our aggregates composed of layers can have layer constitutents that are porous and may in fact have fluids in the pores. We will discuss this case briefly later when we treat fluid permeability for these models, but most of the work along this line – especially in elasticity and poroelasticity of single- and double-porosity heterogeneous media [19, 20] – lies beyond our present scope.

The main point of this effort is to arrive at a set of "models" – by which we mean "effective medium theories" – that are inherently consistent with all the known rigorous bounds. Then we can compute our estimates using these models, and at the same time make rigorous statements about the range of errors likely to be encountered in practice. In fact there may be more than one such model. In some cases we have found a set of closely related models that are dependent on a parameter. Then, if we can somehow characterize the influence and significance of this model parameter, we may be able to make intelligent choices of this "model" based on our limited knowledge of the microstructure of the actual physical system.

We explore these ideas here for transport coefficients. In another paper, we explore fundamentally the same ideas for elastic constants [21].

III. BOUNDS ON TRANSPORT COEFFICIENTS

A. Review of some bounding methods

Because the mathematical structure of the equations is identical, various physical mechanisms such as (for three examples) thermal conductivity, electrical conductivity, and fluid permeability in porous media all require essentially identical treatment at the meso- and macroscales. To emphasize universality, we will not distinguish among these applications as we present this rather general model

study. We will use the symbol σ for conductivity, and we will not specify further which type of conductivity is being considered until later when we consider specific laboratory data on fluid permeability.

Hashin-Shtrikman bounds [22] on conductivity for a multicomponent composite material are well-known to be

$$\sigma_{HS}^{\pm} = \left[\sum_{n=1}^{N} \frac{f_n}{\sigma_n + 2\sigma_{\pm}}\right]^{-1} - 2\sigma_{\pm} \equiv \Sigma(2\sigma_{\pm}), \quad (1)$$

where σ_n is the conductivity in the nth component (nth layer of the laminate) and $\sigma_{\pm}$ are the largest and smallest values of these N conductivities. The second part of Eq. (1) is also taken as the definition of the canonical function Σ for the uncorrelated bounds (and estimates). These bounds are generally improvements on the mean and harmonic mean bounds:

$$\sigma_M = \sum_{n=1}^{N} f_n \sigma_n \qquad \text{and} \qquad \sigma_H = \left[\sum_{n=1}^{N} \frac{f_n}{\sigma_n}\right]^{-1}. \quad (2)$$

For the locally layered aggregate composing the grains of our model, conduction along the symmetry axis is just the series result σ_H, while conduction perpendicular to the symmetry axis is just the parallel result σ_M. These values also correspond to the three eigenvalues of the 3×3 conductivity matrix (occurring once for σ_H and twice for σ_M).

For random polycrystals, there are further results for conductivity that have been reviewed by Helsing and Helte [23]. In particular, the Hashin-Shtrikman bounds [24] for such random polycrystals are determined by

$$\sigma_{HSX}^{\pm} = \Sigma_X(2\sigma_{\pm}), \quad (3)$$

where the canonical function Σ_X for the correlated bounds (and estimates) when applied to correlated (in this case hexagonal crystalline systems) is defined by

$$\Sigma_X(2\sigma_{\pm}) = \left[\frac{1}{3}\left(\frac{1}{\sigma_H + 2\sigma_{\pm}} + \frac{2}{\sigma_M + 2\sigma_{\pm}}\right)\right]^{-1} - 2\sigma_{\pm}, \quad (4)$$

and where $\sigma_+ = \sigma_M$ and $\sigma_- = \sigma_H$. But these are not the most general bounds since they rely on an implicit assumption that the grains are equiaxed.

A more general lower bound that is known to be optimal is due to Schulgasser [25] and Avellaneda *et al.* [26]:

$$\sigma_{ACLMX}^{-} = \Sigma_X(\sigma_{ACLMX}^{-}/2). \quad (5)$$

Note that this bound is usually not written this way (but nevertheless it is not hard to show that this is a correct representation of this bound). We present it this way, in part, because this form emphasizes the analytical similarity of (3) and (5), and it is also convenient for our later efforts at formulating estimates. Note furthermore that the lower Hashin-Shtrikman bound σ_{HSX}^{-} and the Avellaneda *et al.* bound σ_{ACLMX}^{-} actually cross at the value $\sigma_M/\sigma_H = 10$ — with σ_{ACLMX}^{-} being optimal for higher values of the ratio σ_M/σ_H and σ_{HSX}^{-} being for optimal for lower values of the ratio, whenever the equiaxed grains assumption is pertinent.

When the values σ_M and σ_H are treated as the measured values of the conductivity normal and parallel to the symmetry axis of the laminated grains, there are also mean and harmonic mean bounds available based on these values:

$$\sigma_{MX} = \frac{1}{3}\left(\sigma_H + 2\sigma_M\right), \quad (6)$$

and

$$\sigma_{HX}^{-1} = \frac{1}{3}\left(\sigma_H^{-1} + 2\sigma_M^{-1}\right). \quad (7)$$

Of course, these values are less restrictive than the Hashin-Shtrikman bounds, and in fact can be obtained from the canonical function Σ_X in (4) by letting the argument go to ∞ or zero, respectively.

B. Formation factor bounds

1 *Derivation of FF bounds*

The Bergman-Milton [27–34] analytical approach to understanding some general effective transport coefficient σ^* of two-component inhomogeneous media shows that

$$\sigma^* = S(\sigma_1, \sigma_2) = \sigma_1 S(1,0) + \sigma_2 S(0,1) + \int_0^{\infty} \frac{dx\mathcal{S}(x)}{\frac{1}{\sigma_1} + \frac{x}{\sigma_2}}, \quad (8)$$

where $S(1,0)$ and $S(0,1)$ are constants depending only on the geometry and $\mathcal{S}(x) \geq 0$ is a resonance density functional also depending only on the geometry. The integral in (8) is known as a Stieltjes integral [35]. Although the representation (8) has most often been employed to study the behavior of σ^* in the complex plane when σ_1 and σ_2 are themselves complex (corresponding to mixtures of conductors and dielectrics), we will restrict consideration here – as Bergman did in his early work [27] – to pure conductors so that σ_1, σ_2, and σ^* are all real and nonnegative.

In the limit when one or the other of the two constituents is a perfect insulator ($\sigma_i = 0$ for $i = 1, 2$), or in the more common case when one of the constituents is much more strongly conducting than the other, we can define two quantities called formation factors [36] by

$$\lim_{\sigma_1\to\infty} \frac{\sigma^*}{\sigma_1} = \lim_{\sigma_1\to\infty} S(1, \sigma_2/\sigma_1) = S(1,0) = \frac{1}{F_1}, \quad (9)$$

and, similarly, by

$$\lim_{\sigma_2\to\infty} \frac{\sigma^*}{\sigma_2} = \lim_{\sigma_2\to\infty} S(\sigma_1/\sigma_2, 1) = S(0,1) = \frac{1}{F_2}. \quad (10)$$

In a porous material, where solid and pore fluid are each continuously connected throughout the material, both formation factors are finite, and both satisfy $F \geq 1$. The more commonly measured quantity of this type is the electrical formation factor for the continuous fluid component. This measurement may have some complications due to surface conductance [37, 38], but it is usually not contaminated by conductance through the bulk solid material because most rock grains can be correctly assumed to be electrically insulating to a very good approximation. Since the formation factor is strictly a measure of the microgeometry of the heterogeneous medium, it is the same number (except for those possible complications already mentioned of surface electrical conduction [37, 38], which can be eliminated whenever necessary by known experimental and data processing methods) for all mathematically equivalent conductivities. For this presentation, we will use F_1 to represent this formation factor associated with the pore space. On the other hand, for thermal conduction the rock grains are the most highly conducting component and the pore fluids tend to be much more poorly conducting – especially so in the case of saturating air. So, for problems of electrical and thermal conduction, we will take F_2 to be this formation factor associated with the solid frame of the porous material.

To obtain some useful bounds, we again consider the form of (8), now making use of (9) and (10),

$$S(\sigma_1,\sigma_2) = \frac{\sigma_1}{F_1} + \frac{\sigma_2}{F_2} + \int_0^\infty \frac{dx\mathcal{S}(x)}{\frac{1}{\sigma_1}+\frac{x}{\sigma_2}}. \tag{11}$$

For reasons that will become apparent later, we want to compare the values of $S(\sigma_1 + 2\sigma_0, \sigma_2 + 2\sigma_0)$ and $S(\sigma_1,\sigma_2) + 2\sigma_0$, where σ_0 can take any positive value. But σ_0 is limited in the negative range by the restrictions that both $\sigma_1 + 2\sigma_0$ and $\sigma_2 + 2\sigma_0$ must always be nonnegative. A straightforward, but somewhat tedious, calculation shows that

$$S(\sigma_1+2\sigma_0,\sigma_2+2\sigma_0) - S(\sigma_1,\sigma_2) - 2\sigma_0 = \\ 2\sigma_0(\sigma_2-\sigma_1)^2 \int_0^\infty \frac{dxx\mathcal{S}(x)}{(1+x)(\sigma_2+x\sigma_1)[\sigma_2+x\sigma_1+2(1+x)\sigma_0]}. \tag{12}$$

The right hand side of this equation is always positive whenever $\sigma_0 > 0$ and $\sigma_1 \neq \sigma_2$. It vanishes when either $\sigma_0 = 0$ or $\sigma_1 = \sigma_2$. If $\sigma_1 < \sigma_2$, then for negative values of the parameter σ_0, allowed values of σ_0 lie in the range $0 > 2\sigma_0 \geq -\sigma_1$. For these values of σ_0, the right hand side of (12) is strictly negative.

The limiting case obtained by taking $2\sigma_0 \to -\sigma_1$ is most useful because, in this limit, $S(\sigma_1+2\sigma_0,\sigma_2+2\sigma_0) \to (\sigma_2-\sigma_1)/F_2$ — thus eliminating the unknown functional $\mathcal{S}(x)$ from this part of the expression. Then, (12) shows that

$$S(\sigma_1,\sigma_2) \geq \sigma_1 + \frac{\sigma_2-\sigma_1}{F_2} \equiv Q_2(\sigma_1,\sigma_2), \tag{13}$$

which is a general lower bound on $S(\sigma_1,\sigma_2)$ without any further restrictions on the measurable quantities $\sigma_1 \leq \sigma_2$, and F_2.

A second bound can be obtained (again in the limit $2\sigma_0 = -\sigma_1$) by noting that

$$\int_0^\infty \frac{dxx\mathcal{S}(x)}{(1+x)(\sigma_2+x\sigma_1)} \leq \int_0^\infty \frac{dx\mathcal{S}(x)}{\sigma_2+x\sigma_1}, \tag{14}$$

and then recalling [see (11)] that

$$\int_0^\infty \frac{dx\mathcal{S}(x)}{\sigma_2+x\sigma_1} = \frac{1}{\sigma_1\sigma_2}\left[S(\sigma_1,\sigma_2) - \frac{\sigma_1}{F_1} - \frac{\sigma_2}{F_2}\right]. \tag{15}$$

Substituting (14) into (12) produces an upper bound on $S(\sigma_1,\sigma_2)$. By subsequently substituting (15) and then rearranging the result, the final bound is

$$S(\sigma_1,\sigma_2) \leq \sigma_2 + \frac{\sigma_1-\sigma_2}{F_1} \equiv Q_1(\sigma_1,\sigma_2). \tag{16}$$

Comparing (13) and (16), we see consistency requires that

$$\sigma_1 + \frac{\sigma_2-\sigma_1}{F_2} \leq \sigma_2 + \frac{\sigma_1-\sigma_2}{F_1} \tag{17}$$

must be true. Rearranging this expression gives the condition

$$0 \leq (\sigma_2-\sigma_1)\left(1 - \frac{1}{F_1} - \frac{1}{F_2}\right), \tag{18}$$

the validity of which we need to check. In the limit $\sigma_1 = \sigma_2 = 1$, a sum rule follows from (11), and from this we have:

$$1 - \frac{1}{F_1} - \frac{1}{F_2} = \int_0^\infty \frac{dx\mathcal{S}(x)}{1+x} \geq 0. \tag{19}$$

This shows explicitly that (18) is always satisfied as long as $\sigma_2 \geq \sigma_1$. If the inequality $\sigma_2 \geq \sigma_1$ does not hold, then the sense of the bounding inequalities is reversed, so the expressions for the upper and lower bounds are interchanged.

When $\sigma_2 = \text{const}$ and σ_1 varies (as would be expected in a series of either electrical or thermal conductivity experiments with different conducting fluids in the same porous medium), then (13) and (16) are both straight lines that cross at $\sigma_1 = \sigma_2$. The general bounds are therefore

$$\min(Q_1,Q_2) \leq S(\sigma_1,\sigma_2) \leq \max(Q_1,Q_2), \tag{20}$$

where Q_1 and Q_2 were defined in (13) and (16).

A second derivation of the same bounds may provide additional insight into their significance. Again starting from (11), this time we will go directly to the integral term and start making approximations to it. First, consider

$$\int_0^\infty \frac{dx\mathcal{S}(x)}{\frac{1}{\sigma_1}+\frac{x}{\sigma_2}} = \sigma_1\int_0^\infty \frac{dx\mathcal{S}(x)}{1+\frac{x\sigma_1}{\sigma_2}} \geq \sigma_1\int_0^\infty \frac{dx\mathcal{S}(x)}{1+x}, \tag{21}$$

where the inequality holds whenever $\sigma_1 \leq \sigma_2$. Then, similarly, we have

$$\int_0^\infty \frac{dx\mathcal{S}(x)}{\frac{1}{\sigma_1}+\frac{x}{\sigma_2}} = \sigma_2 \int_0^\infty \frac{dx\mathcal{S}(x)}{\frac{\sigma_2}{\sigma_1}+x} \leq \sigma_2 \int_0^\infty \frac{dx\mathcal{S}(x)}{1+x}, \quad (22)$$

again whenever $\sigma_1 \leq \sigma_2$. We can then make use of the identity in sumrule (19) to replace the integral on the far right in both of these expressions. And, finally, applying (21) to (11) gives exactly the lower bound (13), while applying (22) to (11) gives exactly the upper bound (16). All the same comments about reversal of the sense of the inequalities apply here if instead $\sigma_1 \geq \sigma_2$. So, the final result is again (20).

This approach has the advantage that it is clear from the derivation of the inequalities (21) and (22) exactly what approximations have been made in each case to arrive at the bounds on $S(\sigma_1, \sigma_2)$.

Note that there is also another rather obvious lower bound on $S(\sigma_1, \sigma_2)$ obtainable from (11) by simply dropping the integral term involving $\mathcal{S}(x)$. Although this bound has the same asymptotic behavior as $\min(Q_1, Q_2)$, it is easy to see (using the same arguments already presented) that this lower bound is always inferior to $\min(Q_1, Q_2)$ (and especially so when $\sigma_1 \simeq \sigma_2$), thus we need not consider it any further here.

The FF bounds are useful in their own right, but will also be relevant to our model of random polycrystals of laminates in two quite different ways: (1) Assuming a single-phase fluid is present in the pores of a layered porous medium, each layer can be treated as if it has a definite permeability associated with it. If there are only two types of these layers, then for an isotropic random polycrystal the FF bounds are pertinent to estimates of the overall permeability of such a system [34]. For these purposes, it is not important whether the layers themselves have the same or quite different solid materials composing layers and frame. (2) In contrast, for electrical or thermal conductivity, the single-phase fluid is one of the conductors, while the solid material must be the other. Since these bounds are valid for systems having only two conductors present, they can only be used in such cases for estimating the properties of the individual layers of this model — not for the overall transport properties of the macroscale system. So, in the context of the random polycrystals of laminates model, FF bound are most important for the fluid permeability application — which (fortunately) is one of our main interests.

Appendix A discusses two methods of determining formation factors from data, one method based on the formation factor bounds themselves and another using a data differencing technique.

2 *Application of FF bounds*

Warren and Price [39] presented a sophisticated data set that is pertinent to our problem and that can be analyzed quite easily using the formation factor bounds.

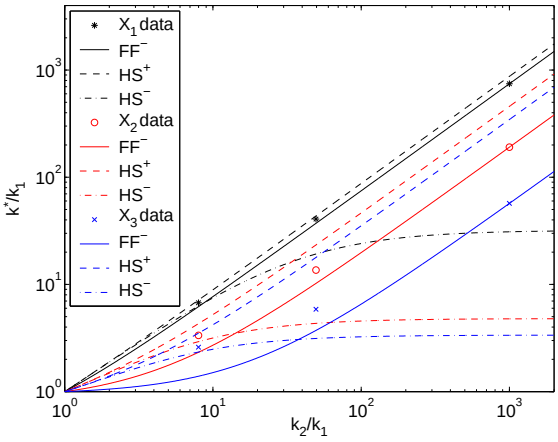

FIG. 1: Rigorous bounds on fluid permeability data of Warren and Price [39] obtained using the upper and lower formation factor bounds from this work, and the upper and lower Hashin-Shtrikman bounds [22]. For X_1 data, $k_2/k_1 \simeq 1000.0$; for X_2 data, $k_2/k_1 \simeq 50.0$; for X_3 data, $k_2/k_1 \simeq 8.0$.

The physical model was composed of a $9 \times 9 \times 9$ cube, containing $9^3 = 729$ porous blocks. Each of these blocks had a well-defined permeability, being approximately one of the four values: 1, 8, 50, 1000 (units unspecified). The smallest permeability was always a constituent of the random porous composite, but the remaining volume filler was always chosen from just one of the other three types. So there were three distinct binary (X/Y) composites studied: 8/1, 50/1, and 1000/1. Furthermore, there were only four distinct volume fractions used, and these came in pairs: one pair being $f_1 = 0.088$ and $f_1 = 0.912$ and the other pair being $f_1 = 0.441$ and $f_1 = 0.559$. Since these pairs sum to unity, this means that to a very good approximation the two relevant formation factors were effectively interchanged within each of these types of data sets, each porous component being occupied in an X/Y composite once by X and once by Y. This means that phase interchange relationships [40, 41] can also be tested within the context of this experiment, if so desired.

Bounds obtained by first estimating the F_1 and F_2 formation factors from the Warren and Price data (see TABLE 1) are illustrated in Figure 1 along with the upper and lower Hashin-Shtrikman bounds for comparison. The Hashin-Shtrikman bounds depend only on known volume fractions and constituent conductivities. Figure 1 clearly shows that the Hashin-Shtrikman bounds provide fairly tight upper bounds all the time. The HS lower bounds are best at low values of the permeability ratio k_2/k_1. They diverge from the data at higher values, as they must since they do not incorporate the fact that the formation factors of both components are finite. The formation factor bounds on the other hand give excellent results for the lower bounds at all values of k_2/k_1. In fact they agree exactly in this case with the measured values for the highest value of k_2/k_1, which is of course unrealistic, but a natural result of the way the forma-

tion factors were themselves estimated from this data set. The true formation factor F_2 is actually just slightly larger than the lower bound given in TABLE 1. But, since $k_2/k_1 \simeq 1000.0$, we assume that the error made here is small, and also of the same order as the experimental errors in these measurements.

IV. ESTIMATES FOR TRANSPORT COEFFICIENTS

A. Standard estimates

Two geometric means of interest for conductivity of the random polycrystals of laminates model are:

$$\sigma_{G1} = \prod_{n=1}^{N} \sigma_n^{f_n}, \tag{23}$$

which is the geometric mean based on the volume fractions f_n, and

$$\sigma_{G2} = \left(\sigma_H \sigma_M^2\right)^{1/3}, \tag{24}$$

which is the geometric mean based on measurements of the principle conductivities of the individual anisotropic grains making up the polycrystalline composite. Clearly, σ_{G1} takes no account of the fine structure of the medium, and should be thought of as an uncorrelated estimate, while σ_{G1} does take account of the fine structure and is therefore a correlated estimate.

Coherent potential approximations (CPA) [42] or self-consistent estimates [3, 4, 43, 44] are easily obtained from (1) and (3). Because the functionals involved in the statement of the bounds are very well-behaved — being monotonic functions of their scalar argument, it is easy to show that some intermediate value of the conductivity sought must exist that has the same value (usually within some scalar constant value, which in this case is 2) as the argument of the functional. The uncorrelated CPA estimate is then given by

$$\sigma_{CPA}^* = \Sigma(2\sigma_{CPA}^*). \tag{25}$$

Similarly, the correlated CPA estimate for random aggregates of hexagonal crystals is [23]

$$\sigma_{CPAX}^* = \Sigma_X(2\sigma_{CPAX}^*). \tag{26}$$

B. A new class of estimators

Comparing the lower bound (5) and the CPA estimate (26), we see that they share the functional relationship

$$\sigma_X^*(P) \equiv \Sigma_X(P\sigma_X^*(P)), \tag{27}$$

with $P = 1/2$ for the rigorous lower bound (5) and $P = 2$ for the CPA estimate (26). It seems clear from prior work (and we will show this here in some detail) that a new class of approximations or estimates can be obtained by permitting the parameter P to span the range $1/2 \le P \le 2$. We have found that $P \simeq 1$ is one useful intermediate choice, and that this choice seems to agree well with data at least as well as the choice $P = 2$ justified by using the CPA. Clearly, (27) also automatically has the sought for characteristic that it always produces estimates inside the known rigorous bounds for these correlated media as long as $1/2 \le P \le 2$.

We can also consider a similar estimator for

$$\sigma^*(P) \equiv \Sigma(P\sigma^*(P)), \tag{28}$$

for isotropic random composites composed of "uncorrelated" isotropic constituents. In this case, the best simple lower bound having the correct functional form is the Hashin-Shtrikman bound [22]

$$\sigma^* \ge \sigma_{HS}^- = \Sigma(2\sigma_-). \tag{29}$$

Thus, because of the monotonicity properties of Σ, (28) will always lie between the rigorous bounds if $2\sigma_- \le P\sigma^*(P) \le 2\sigma_{CPA}^*$, since the CPA estimator is always within the bounds, and very often a high estimator (consistently too high) for real data.

Since it is known that the correlated bound σ_{ACLMX}^- crosses the Hashin-Shtrikman lower bound, it is reasonable to expect the same might happen with our uncorrelated estimator. In fact it is not hard to show that when one conductivity is much greater than the other so that $\sigma_+ \gg \sigma_-$, then

$$\sigma_{HS}^- \simeq \frac{\sigma_-(3 - 2f_-)}{f_-} \tag{30}$$

and

$$\sigma^*(P) \simeq \frac{\sigma_-}{[f_-(1+P) - P]}. \tag{31}$$

Equating these expressions, we find that the two cross at the points

$$f_- = \frac{3}{4} \quad \text{and} \quad 1 \qquad \text{for} \qquad P = 1, \tag{32}$$

and

$$f_- = \frac{1}{2} \quad \text{and} \quad 1 \qquad \text{for} \qquad P = \frac{1}{2}. \tag{33}$$

Thus, for high contrast transport problems, we expect these two curves to cross when the high conductivity material occupies about 25% of the total volume for $P = 1$ and at about 50% for $P = 1/2$.

Numerical examples are presented in the following section. Some other details of the behavior of both of the new estimators are presented in Appendix B.

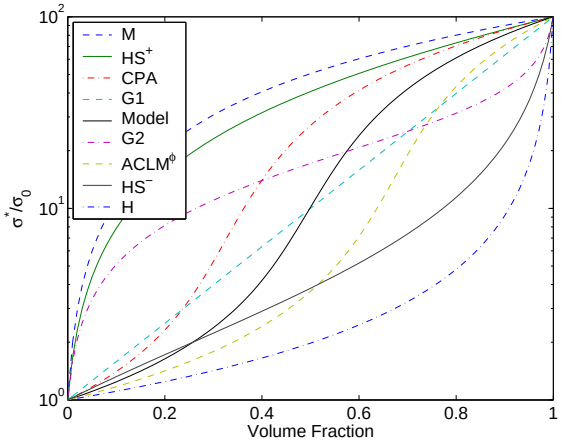

FIG. 2: Uncorrelated bounds and estimates on conductivity assuming that volume fraction information is available, but it is not known that the medium is composed of laminated grains. Two geometric means [G1 and G2 – see Eqs. (23) and (24)] are presented to permit some direct comparisons with Figure 2. Here Model means (28) with $P = 1$, and ACLM$^{\phi}$ means the same equation with $P = 1/2$.

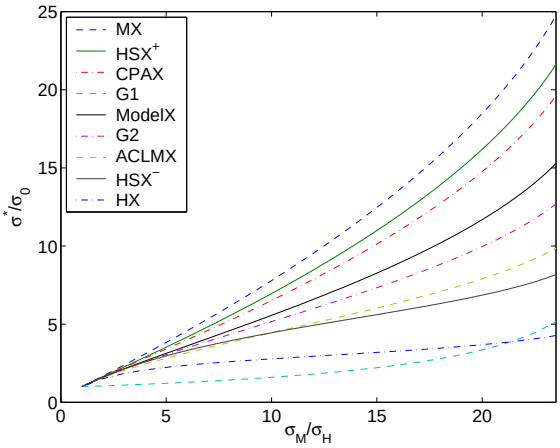

FIG. 3: Same as Figure 2 for correlated bounds and estimates based on random polycrystalline microstructure formulas. For this Figure it is assumed that the volume fractions of the microstructural components are unknown, but measurements have been made instead on the conductivities parallel and perpendicular to the symmetry axis of a typical (laminated) grain. All calculations here differ from those of Figure 2 except for the two geometric means, both of which are exactly the same values as those plotted in Figure 2. Here ModelX means (27) with $P = 1$, and ACLMX means the same equation with $P = 1/2$.

V. EXAMPLES AND DISCUSSION

A. Random polycrystals of laminates

Figures 2 and 3 summarize the relationships among the various bounds and effective medium estimators discussed already in the text. Figure 2 shows explicitly how the various estimators perform as a function of volume fraction for the random polycrystals of laminates model. The geometric mean G1 [Eq. (23)] is a straight line across this log-linear plot. This geometric mean has sometimes been claimed to be a very good estimator of some types of data [39, 45]. This plot shows that it is true that G1 falls in the middle of the group, and this is reasonable if the medium is in fact essentially uncorrelated in space. But, in contrast, Figure 3 shows in a very startling way that when significant correlations are present, the mean G1 is a very poor estimator, as it lies below the lowest bound plotted here over most of the range of the plot. Thus, G2 [Eq. (24)] is the better estimator of these geometric means — at least for this correlated case.

The models ACLM$^{\phi}$ (P=1/2) and Model (P=1) used in Figure 2 both fall below the lower Hashin-Shtrikman bound in the range of volume fractions $f_- > 1/2$ and $f_- > 3/4$, respectively, and so they might not be considered useful in this region. However, the quantitative differences in this range for $P = 1$ are actually very small (on the order of the line width as seen later in the Figure 4), and also very close to the data. So this theoretical flaw may be considered negligible for some purposes of data comparison. The CPA is always inside the Hashin-Shtrikman bounds, but it is generally quite a bit higher than the geometric mean G1 for most of the range of the high range volume fractions, and therefore is certainly not going to agree with data that are seen to lie close to the geometric mean G1. The compromise using $P = 1$ seems to be the best choice of a model in the absence of information about spatial correlations, but it can be replaced by the HS lower bound if desired below $f_+ = 0.25$ as seen in this Figure.

For correlated media of the type under consideration here, Figure 3 shows that ModelX (P=1) falls nicely between the CPAX and ACLMX curves as it should, and is also a fair approximation to the G2 geometric mean, which also falls within the same domain.

B. Fluid permeability data comparisons

Figure 4 presents a theory-to-data comparison for the Warren and Price [39] data set on fluid permability. Although arguments of Warren and Price seem to favor the geometric mean G1 as a general descriptor of these types of data, we see that G1 is only very crudely measuring the behavior over the full range of volume fraction. The CPA and Mod (P=1) estimators both do a much better job of following the trends in the data, than does G1. But CPA is again observed to be too high essentially all of the time. The choice $P = 1$ seems to be the more conservative estimator, being about right at the extremes of volume fraction, and somewhat too low for the mid-region. This suggests that a better estimator might involve nonconstant choices of P, being close to unity at the extremes of volume fraction and somewhere between

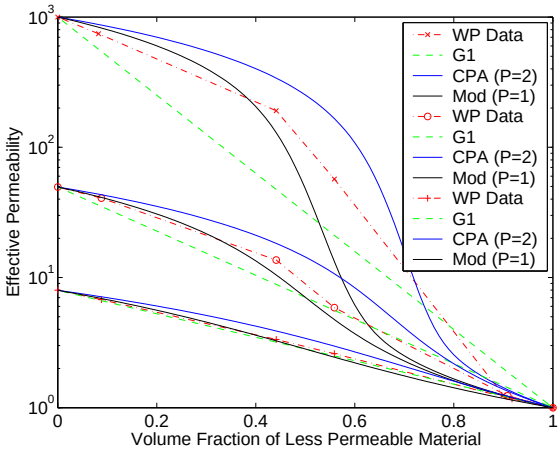

FIG. 4: Fluid permeability data of Warren and Price [39] are compared to various models: (1) the geometric mean G1 defined in Eq. (23), (2) the CPA self-consistent effective medium theory with $P = 2$, and (3) the new model with the different parameter choice $P = 1$. The geometric mean gives only very crude agreement except for the case $k_2/k_1 \simeq 8.0$, where all three medthods do about equally well. In general the CPA is too high. The new model does seem to capture most of the overall trend in the data in all three example data sets, especially so at the extremes of volume fraction; but the model is generally too low in the mid-region.

1 and 2 in the middle range.

To provide some physical justification for this new model, consider that choosing $P \neq 2$ provides a means of taking into account imperfections in the heterogeneous medium. It is known [4] that for resistor networks the factor equivalent to P in the standard CPA approximation actually depends on the coordination number z at every node: so $P = z/3 - 1$. Typically, $z = 6$ in 3D, so $P = 2$. If the coordination number is less than six, as it typically would be in two dimensions, or if there are defects in the network, then an overall effective value of P less than 2 is expected. So we might take the best fitting value of P when trying to fit data with such a model as a measure of the defects in the heterogeneous (or, in the Warren and Price case, porous) medium being studied. For very discrete models like the ones constructed in the laboratory by Warren and Price, we expect there to be more defects of this type at the high and low volume fractions because it is easier for individual blocks of the minority constituent to be completely surrounded by those of the majority constituent. In the middle range of volume fraction, this sort of complete isolation (a type of localization effect) of one of the block types probably happens only very rarely. So this argument provides one possible physical reason for the observed behavior in these porous materials in the mid-range of volume fractions.

VI. CONCLUSIONS

In the history of studies of heterogeneous media, the very earliest work on electrical, elastic, and viscous media [1–3, 46–48] involved ad hoc procedures intended to provide sensible estimates of the physical constants of interest in such systems. Much later, work on bounding methods first showed that some of the known estimates were in fact rigorous bounds [12] and subsequently produced quite accurate and useful bounds [49, 50] that were then proven to be optimal in the sense that for certain special classes of microstructures the bounding values could be attained. Later still it was established that certain choices of these *ad hoc* estimates (or effective medium theories) had special relationships to the bounds [5–7]. In particular, some of these estimates were shown always to lie between the rigorous upper and lower bounds on the material constants [5–7, 51, 52].

Rigorous bounds designed to improve on mean and harmonic mean bounds, and/or Hashin-Shtrikman bounds usually require some knowledge of the microstructure of the composite. One common (usually theoretical) method of quantifying the microstructure is by specifying/measuring spatial correlation functions [53–55]. But other methods are possible, and sometimes more practical. As emphasized here, the formation factor bounds incorporate the microstructural information about a porous medium in a very different way, yet produce useful bounds — comparable to and in some cases (especially for high contrast media) improving on the Hashin-Shtrikman bounds. If both formation factors in a two-component composite are finite, then at least some paths are percolating (connected) throughout the medium for both constituents. This fact is a powerful theoretical, and very practical quantitative, statement about the microstructure and, in particular, about the long-range order of the composite.

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TABLE 1. Lower bounds on the formation factors F_1 and F_2 in the fluid permeability data of Warren and Price [39], as determined by using the formation factor bounds. Volume fractions of the porous component number 1 are given by f_1.

f_1	F_1^-	F_2^-
0.088	3966.0	1.343
0.441	17.830	5.264
0.559	5.264	17.830
0.912	1.343	3966.0

APPENDIX A: ESTIMATING FORMATION FACTORS FROM DATA

Two methods of estimating formation factors from data are presented here: One uses the formation factor bounds to estimate the formation factors present in a data set. This approach has been found to be quite useful for small data sets (an example is shown here in Figure 1). The second method is a data differencing method. This method is not as good for small data sets as the formation factor bounding approach, but for large data sets it provides a methodical means of eliminating the influence of the resonance density functional on the formation factor estimator.

A.1: Using formation factor bounds

When the formation factors have been measured, the formation factor bounds supply estimates (upper and lower bounds) on the expected values of the conductivities of the system as the component conductivities are varied. When the formation factors have not been measured independently, they can also be estimated from other data using these same bounds.

From Eqs. (13) and (16), we can easily infer (assuming only $\sigma_2 > \sigma_1$) that

$$F_2 \geq \frac{\sigma_2 - \sigma_1}{S(\sigma_1, \sigma_2) - \sigma_2}, \tag{34}$$

and similarly

$$F_1 \geq \frac{\sigma_2 - \sigma_1}{\sigma_2 - S(\sigma_1, \sigma_2)}. \tag{35}$$

These bounds can then be applied in turn to each measured data point $S(\sigma_1, \sigma_2)$. Having done this to the entire data set, then the largest value in each case is the preferred lower bound on the formation factor. This process has been carried through on the Warren and Price data set [39] and the results obtained are quoted in TABLE 1. These values were then used to produce the formation factor bounds shown in Figure 1.

A.2: Data differencing scheme

Suppose we have just three independent measurements of the conductivity $S(\sigma_1, \sigma_2)$, for fixed σ_1 and the values σ_2^A, σ_2^B, σ_2^C for the second conductivity variable. Then, from (11) it is easy to show that

$$\frac{\sigma_2^C S(\sigma_1,\sigma_2^B) - \sigma_2^B S(\sigma_1,\sigma_2^C)}{\sigma_2^C - \sigma_2^B} = \frac{\sigma_1}{F_1} + \sigma_1 \int_0^\infty \frac{dx\mathcal{S}(x)}{(1+x\sigma_1/\sigma_2^B)(1+x\sigma_1/\sigma_2^C)}. \tag{36}$$

The advantage of this formula is that the integral now contains a second positive factor in the denominator that tends to reduce the influence of this contribution to the right hand side. When there are three measurements, there are three such first order differences available. But in addition there is also one second order difference available, namely:

$$\sigma_2^A \frac{\sigma_2^C S(\sigma_1,\sigma_2^B) - \sigma_2^B S(\sigma_1,\sigma_2^C)}{(\sigma_2^A - \sigma_2^C)(\sigma_2^C - \sigma_2^B)} - \sigma_2^C \frac{\sigma_2^A S(\sigma_1,\sigma_2^B) - \sigma_2^B S(\sigma_1,\sigma_2^A)}{(\sigma_2^A - \sigma_2^C)(\sigma_2^C - \sigma_2^B)} = \frac{\sigma_1}{F_1} + \sigma_1 \int_0^\infty \frac{dx\mathcal{S}(x)}{(1+x\sigma_1/\sigma_2^A)(1+x\sigma_1/\sigma_2^B)(1+x\sigma_1/\sigma_2^C)}. \tag{37}$$

For this expression the integral contribution has clearly been reduced more than for the first order differences. The reduction achieved this way is greatest when the various ratios σ_1/σ_2^A, etc., are as large as possible. So either small values or many values of σ_2 are most useful for the application of this method. Neither of these options was available in the Warren and Price [39] data set, so this method (although it was tried) did not turn out to be as useful as the formation factor bounding method described already. Note also that this method produces only estimates for F_1, whereas the formation factor bounds produce estimates for both F_1 and F_2.

Clearly this process of magnitude reduction can also be continued when more than three data values are available. With many data values, this method should become viable for estimating F_1.

APPENDIX B: EXAMPLES OF $\sigma_X^*(P)$ AND $\sigma^*(P)$

Two types of new estimators are considered: first, the estimator $\sigma_X^*(P)$ for random polycrystals and, second, the estimator $\sigma^*(P)$ for random composites of isotropic constituents. These estimators are both guaranteed to lie between the bounds if certain restrictions are placed on the parameter P: for σ_X^*, $1/2 \leq P \leq 2$, while, for σ^*, the requirements are $2\sigma_- \leq P\sigma^* \leq 2\sigma^*$.

B.1: Random polycrystal estimators

Formula (27) for the correlated $\sigma_X^*(P)$ may be rewritten as

$$\frac{1}{\sigma_X^*} = (1+P)\frac{1}{3}\left(\frac{1}{\sigma_H + P\sigma_X^*} + \frac{2}{\sigma_M + P\sigma_X^*}\right). \quad (38)$$

It is easy to see that this is just a quadratic equation for σ_X^*. The general solution of this equation is

$$\sigma_X^* = \frac{1}{2P}\left(-Z_X \pm \sqrt{Z_X^2 + 4P\sigma_H\sigma_M}\right), \quad (39)$$

where

$$Z_X = \frac{1}{3}\left[(1-2P)\sigma_M + (2-P)\sigma_H\right]. \quad (40)$$

An important special case is

$$P \equiv \frac{2\sigma_H + \sigma_M}{\sigma_H + 2\sigma_M}, \quad (41)$$

which gives precisely $Z_X = 0$ and $\sigma_X^* = \sqrt{\sigma_H\sigma_M/P}$. Note that $P \leq 1$ when it is given by (41), so $\sigma_X^* \geq \sqrt{\sigma_H\sigma_M}$ for this special case.

Assuming $\sigma_H \ll \sigma_M$, some examples of approximate evaluations of (39) are:

$$\sigma_X^* \simeq \sqrt{\sigma_H\sigma_M/P} + O(\sigma_H) \quad \text{for} \quad P = \frac{1}{2}, Z_X \simeq O(\sigma_H), \quad (42)$$

$$\sigma_X^* \simeq \frac{\sigma_M}{3} + O(\sigma_H) \quad \text{for} \quad P = 1, \quad (43)$$

$$\sigma_X^* \simeq \frac{\sigma_M}{2} + O(\sigma_H) \quad \text{for} \quad P = 2. \quad (44)$$

Without restrictions on σ_H,

$$\sigma_X^* \to \frac{1}{3}\left(\sigma_H + 2\sigma_M\right) \quad \text{for} \quad P \to \infty, \quad (45)$$

which is the same as σ_{MX}. It also follows immediately from (38) that

$$\sigma_X^* \to \left[\frac{1}{3}\left(\frac{1}{\sigma_H} + \frac{2}{\sigma_M}\right)\right]^{-1} \quad \text{for} \quad P \to 0, \quad (46)$$

which is σ_{HX}.

B.2: Estimators for random composites of isotropic constituents

By analogy to the definition of the estimator $\sigma_X^*(P)$, we also define the corresponding concept for uncorrelated random heterogeneous media composed of isotropic constituents: $\sigma^*(P)$.

This estimator can be defined for an arbitrary number of constituents. But to maintain, and also emphasize, the analogy to the previous case, we will restrict the discussion here to just two constituents. Formula (28) for the uncorrelated estimator $\sigma^*(P)$ may then be rewritten as

$$\frac{1}{\sigma^*} = (1+P)\left(\frac{f_1}{\sigma_1 + P\sigma^*} + \frac{f_2}{\sigma_2 + P\sigma^*}\right). \quad (47)$$

It is easy to see that, like (38), this is just a quadratic equation for σ^*. The general solution of this equation is

$$\sigma^* = \frac{1}{2P}\left(-Z \pm \sqrt{Z^2 + 4P\sigma_1\sigma_2}\right), \quad (48)$$

where

$$Z = \left[(f_1 - f_2P)\sigma_2 + (f_2 - Pf_1)\sigma_1\right]. \quad (49)$$

Again, an important special case is found to be

$$P \equiv \frac{f_1\sigma_2 + f_2\sigma_1}{f_1\sigma_1 + f_2\sigma_2} = \frac{\sigma_1\sigma_2}{<\sigma><1/\sigma>^{-1}}, \quad (50)$$

which gives precisely $Z = 0$ and $\sigma^* = \sqrt{\sigma_1\sigma_2/P} = \sqrt{\sigma_H\sigma_M}$.

Assuming $\sigma_1 \ll \sigma_2$ and $f_1 \neq f_2$, some examples of approximate evaluations of (48) are:

$$\begin{aligned}\sigma^* &= \tfrac{1}{2P}\left[\sqrt{(1-P)^2\sigma_1^2 + 4P\sigma_1\sigma_2} - (1-P)\sigma_1\right] \\ &\simeq \sqrt{\sigma_1\sigma_2/P} + O(\sigma_1) \quad \text{for} \quad P = \tfrac{f_1}{f_2}, Z = (1-P)\sigma_1,\end{aligned} \quad (51)$$

$$\begin{aligned}\sigma^* = \sqrt{\sigma_1\sigma_2 + (f_1-f_2)^2(\sigma_1-\sigma_2)^2/4} \\ -(f_1-f_2)(\sigma_2-\sigma_1)/2 \quad \text{for} \quad P = 1,\end{aligned} \quad (52)$$

and

$$\begin{aligned}\sigma^* = \tfrac{1}{2P}\left[\sqrt{(1-P)^2\sigma_2^2 + 4P\sigma_1\sigma_2} - (1-P)\sigma_2\right] \\ \text{for} \quad P = \tfrac{f_2}{f_1}, Z = (1-P)\sigma_2.\end{aligned} \quad (53)$$

All three of these estimators give exactly the geometric mean $\sqrt{\sigma_1\sigma_2}$ when $f_1 = f_2$, so $P = 1$. Otherwise, all three of these estimators depend strongly on f_1 and f_2, and in particular two depend on the sign of $1 - P$.

Without restrictions on σ_1,

$$\sigma^* \to (f_1\sigma_1 + f_2\sigma_2) \quad \text{for} \quad P \to \infty, \quad (54)$$

which is $<\sigma> = \sigma_M$. It also follows immediately from (47) that

$$\sigma^* \to \left(\frac{f_1}{\sigma_1} + \frac{f_2}{\sigma_2}\right)^{-1} \quad \text{for} \quad P \to 0, \quad (55)$$

which is $<1/\sigma>^{-1} = \sigma_H$.

Discussion of the significance of the various P values relative to the rigorous bounds is given in the main text.

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